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Study of the interconversion between viscoelastic behaviour functions of PMMA

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Abstract The use of polymers and polymer-based composites in mechanical, civil and electronic engineering has been growing owing to advances in the technology of materials. The different applications and working conditions of these materials require knowledge about their viscoelastic material functions: relaxation modulus, compliance, complex modulus, etc. Interconversion between these functions may be required for different reasons such as the impossibility of direct experimentation under certain excitation conditions. In this work, a DMA is used to calculate the experimental viscoelastic functions of a linear viscoelastic material (PMMA). The same functions are estimated by interconversion methods and compared with experimental ones. The results show that the interconversion functions fit properly the experimental functions.

Keywords Polymers · Mechanical characterization · Viscoelasticity · Interconversions

1 Introduction

Field studies of viscoelastic materials have been on the increase in recent years due, among other factors, to a greater use of polymeric or polymer-based materials, new applications for woods, or advances or more stringent demands for materials used in the field of biomechanics.

To use these materials in engineering calculations, they must first be correctly characterized and, in most cases, this differs greatly from the classical study of linear elastic materials. One essential characteristic of viscoelastic materials is the time- and temperature-dependence of their mechanical properties, such as the relaxation modulus, $E(t)$, Poisson's coefficient $\mu(t)$ or the volumetric modulus, $K(t)$. Owing to these changes in properties, it is complicated to achieve a correct characterization of the material. There are 12 different

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Table 1 Type of moduli for viscoelastic materials

Moduli	Time		Frequency	
	Relaxation	Creep	Relaxation	Creep
Shear	$G(t)$	$J(t)$	$G^*(\omega)$	$J^*(\omega)$
Bulk	$K(t)$	$B(t)$	$K^*(\omega)$	$B^*(\omega)$
Uniaxial	$E(t)$	$D(t)$	$E^*(\omega)$	$D^*(\omega)$
Poisson coef.	$\mu_r(t)$	$\mu_f(t)$	$\mu_r^*(\omega)$	$\mu_f^*(\omega)$

viscoelastic moduli that are interrelated and at least two of them must be determined to obtain a viscoelastic characterization of the material. These functions respond to the different types of solicitation imposed on the material:

a) Stress relaxation and creep moduli, a constant deformation or stress is applied to the material, respectively.
b) Static moduli (time domain) and complex moduli (frequency domain), if the load is static or oscillatory.
c) Uniaxial, shear or bulk moduli, if the solicitation corresponds to the application of uniaxial loads, shear or bulk.

The names of the different behavior functions and their respective Poisson's coefficients are shown in Table 1.

In most situations, it is not feasible to carry out all the experiments that define the behavior of a material, owing to a need to reduce costs or limitations of time, test equipment or even insufficient study material. For this reason, at least one of the solicitations listed in Table 1 is usually omitted. The interconversion functions between the different moduli of the material are, therefore, an important tool in viscoelasticity studies.

An important group within the viscoelastic materials corresponds to those that present linear viscoelastic behavior (Tschoegl 1989). For these materials, it is relatively simple to apply a range of methods to resolve the equations that relate the different functions (Emri et al. 2005; Park and Schapery 1999a, 1999b; Lakes and Wineman 2006; Tschoegl et al. 2002; Sorvari and Malinen 2007).

Interconversion functions can be classified according to the criteria given in Table 1. In other words, depending on the type of load applied (axial, shear or bulk), the type of test carried out (stress relaxation or creep) and on whether the load is static or dynamic.

In the case of interconversions based on the type of axial load, shear or bulk, the relationships between the moduli of a linear elastic material are well defined and can be obtained by applying the correspondence principle (Shames and Cozzarelli 1997; Lakes 1998). As a result, if any two moduli of the material are known, the remaining ones can be determined. For this type of reconversion it is recommendable, because of its relative simplicity, to obtain experimentally the axial modulus of static relaxation and Poisson's coefficient (Lakes and Wineman 2006), by estimating both of them from the same specimen during the same experiment (Tschoegl et al. 2002).

In cases of interconversions based on the type of test, stress relaxation or creep, and depending on the static or dynamic nature of the load, in spite of having integral expressions that relate the viscoelastic functions, it is not easy to find their exact solution. For this reason, alternative methods of interconversion have been developed, such as application of the generalized methods of Maxwell and Kelvin, or even experimental interconversion methods (Ninomiya and Ferry 1959). The scope or limitations of each method depend on the theoretical substrate and the assumptions and simplifications adopted in each case.

Although the theoretical study of the different interconversion methods is well-documented in the specialist literature (Tschoegl 1989; Emri et al. 2005; Park and Schapery 1999a, 1999b; Lakes and Wineman 2006; Tschoegl et al. 2002; Sorvari and Malinen 2007; Shames and Cozzarelli 1997; Lakes 1998; Ninomiya and Ferry 1959), it is not easy to find experimental data to estimate the error made when used these methods. The aim of this work is, therefore, to obtain the experimental axial moduli in cases of relaxation (static and dynamic) and creep (static) for a linear viscoelastic material and to compare them with moduli deduced analytically from the interconversions.

2 Theoretical analysis

The different interconversions between the viscoelastic functions or relaxation and creep moduli and also between the moduli obtained in static and dynamic tests, are based on the constitutive integrals of linear viscoelasticity (Lakes 1998):

$$\sigma(t) = \int_0^t E(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \tag{1}$$

$$\varepsilon(t) = \int_0^t D(t-\tau)\frac{\partial\sigma(\tau)}{\partial\tau}d\tau \tag{2}$$

From (1) and (2) the following relationship between the relaxation modulus $E(t)$ and the creep modulus $D(t)$ can be established:

$$\int_0^t E(t-\tau)\frac{dD(\tau)}{d\tau}d\tau = 1 \tag{3}$$

The operational moduli, obtained by means of the s-Laplace transform, corresponding to $E(t)$ and $D(t)$, are defined as:

$$\tilde{E}(s) = s\int_0^\infty E(t)e^{-st}dt \tag{4}$$

$$\tilde{D}(s) = s\int_0^\infty D(t)e^{-st}dt \tag{5}$$

By combining (3) with (4) and (5) the following relationship between the operational moduli is obtained:

$$\tilde{D}(s)\tilde{E}(s) = 1 \tag{6}$$

Similarly, the operational moduli and complex moduli produced by oscillating loads, can be related (Tschoegl 1989) by the following expressions:

$$E^*(\omega) = \tilde{E}(s)|_{s\to i\omega} \tag{7}$$

$$D^*(\omega) = \tilde{D}(s)|_{s\to i\omega} \tag{8}$$

where $E^*(\omega)$ is the complex modulus and $D^*(\omega)$ is the complex flexibility modulus.

Finally, by substituting expressions (7) and (8) in (6) the principal equation for interconversion between dynamic tests is obtained.

$$E^*(\omega)D^*(\omega) = 1 \tag{9}$$

2.1 Conversion of static to dynamic moduli: Prony coefficients method

This method is based on the fact that the parameters of the Prony series (Chen 2000), obtained by fitting the experimental data of the relaxation modulus using a generalized Maxwell and the creep modulus by a generalized Kelvin model, can be used to generate the curves of the respective complex moduli.

The respective equations for the generalized Maxwell and Kelvin moduli are as follows:

$$E(t) = E_\infty + \sum_{i=1}^{m} e_i \exp\left(-\frac{t}{\rho_i}\right) \tag{10}$$

$$D(t) = D_0 + \sum_{j=1}^{n} d_j \left(1 - \exp\left(-\frac{t}{\tau_j}\right)\right) \tag{11}$$

where, e_i and ρ_i are the Prony series coefficients for the relaxation and d_j and τ_j are the Prony series creep coefficients.

From these equations, the operational moduli defined previously with (4) and (5) can be constructed:

$$\tilde{E}(s) = E_\infty + \sum_{i=1}^{m} \frac{s\rho_i e_\mathrm{i}}{s\rho_i + 1} \tag{12}$$

$$\tilde{D}(s) = D_0 + \sum_{j=1}^{n} \frac{d_j}{s\tau_j + 1} \tag{13}$$

Taking into account expressions (7) and (8), the complex moduli can be calculated from the real part (storage modulus) and the imaginary part (loss modulus), through the following expressions:

$$E'(\omega) = E_\infty + \sum_{i=1}^{m} \frac{\rho_i^2\omega^2 e_i}{\rho_i^2\omega^2 + 1} \tag{14}$$

$$E''(\omega) = \sum_{i=1}^{m} \frac{\rho_i\omega e_i}{\rho_i^2\omega^2 + 1} \tag{15}$$

$$D'(\omega) = D_0 + \sum_{j=1}^{n} \frac{d_j}{\tau_j^2\omega^2 + 1} \tag{16}$$

$$D''(\omega) = \sum_{j=1}^{n} \frac{d_j\tau_j\omega}{\tau_j^2\omega^2 + 1} \tag{17}$$

with which the complex modulus and the complex flexibility modulus can be calculated from the Prony series of the relaxation and creep moduli, respectively.

2.2 Conversion between static moduli: Park–Schapery method

The Park–Schapery method (Park and Schapery 1999a) is based on direct resolution of the integral (3) using the generalized models of Maxwell and Kelvin for $E(t)$ and $D(t)$ respectively. Substituting the equations of both models in (3), the following equation is obtained:

$$\int_0^t \left(E_\infty + \sum_{i=1}^{m} e_i \cdot \exp\left(-\frac{t-\tau}{\rho_i}\right)\right) \cdot \left(D_0\delta(\tau) + \sum_{j=1}^{n} \frac{d_j}{\tau_j} \cdot \exp\left(-\frac{\tau}{\tau_j}\right)\right) d\tau = 1 \qquad (18)$$

If one of the groups of constants $\{\rho_i, E_\infty$ and $e_i\ \ (i = 1, \dots, m)\}$ or $\{\tau_j, D_0$ and $d_j\ \ (j = 1, \dots, n)\}$ are known, the coefficients of the objective Prony series can be obtained by resolving a linear system of algebraic equations, from the analytical solution of (18).

If $D(t)$ is to be found from $E(t)$, then the system of equations is:

$$A_{kj} d_j = B_k \qquad (19)$$

where:

$$A_{kj} = E_\infty\left(1 - \exp\left(-\frac{t_k}{\tau_j}\right)\right) + \sum_{i=1}^{m} \frac{\rho_i e_i}{\rho_i - \tau_j}\left(\exp\left(-\frac{t_k}{\rho_i}\right) - \exp\left(-\frac{t_k}{\tau_j}\right)\right)$$

$$B_k = 1 - D_0\left(E_\infty + \sum_{i=1}^{m} e_i \cdot \exp\left(-\frac{t_k}{\rho_i}\right)\right)$$

and t_k $(k = 1, \dots, p)$ is the vector of discrete times, the values of which correspond to the upper integral limit of (3). To select the time constants, t_k, the collocation method proposed by Schapery (1961) can be used, where these constants are usually specified adequately instead of being calculated (Park and Schapery 1999a). By assuming $p = n$, it is recommended to select $t_k = a\tau_k$ for $a = 1$ or $a = 1/2$ whereby the last one is considered here. Hence, in t_k time, (3) is satisfactory fulfilled. The glassy compliance, D_0, is given by Park and Schapery (1999a):

$$D_0 = \frac{1}{E_\infty + \sum_1^m e_i} \qquad (20)$$

To obtain $E(t)$ from $D(t)$, the Prony relaxation parameter vector must be worked out, giving the system:

$$A_{ki} e_i = B_k \qquad (21)$$

where e_i is the searched Prony parameter vector for relaxation and:

$$A_{ki} = D_0\left(\exp\left(-\frac{t_k}{\rho_i}\right) - 1\right) + \sum_{j=1}^{n} \frac{\tau_j d_j}{\rho_i - \tau_j}\left(\exp\left(-\frac{t_k}{\rho_i}\right) - \exp\left(-\frac{t_k}{\tau_j}\right)\right)$$

$$B_k = 1 - E_\infty\left(D_0 + \sum_{j=1}^{n} d_j \cdot \left(1 - \exp\left(-\frac{t_k}{\tau_j}\right)\right)\right)$$

where the vector of discrete times t_k is obtained as $t_k = a\rho_k$, with $p = m$ and $a = 1/2$, and the equilibrium modulus E_∞ is given by Park and Schapery (1999a):

$$E_\infty = \frac{1}{D_0 + \sum_1^n d_j} \tag{22}$$

2.3 Conversion from dynamic to static moduli: Ninomiya and Ferry algorithms

Direct resolution in this case, or resolution using models, such as that of Maxwell or Kelvin, which do not have satisfactory fits, is complex. It is, therefore, more frequent to use other algorithms such as the experimental Ninomiya and Ferry algorithm (Ninomiya and Ferry 1959), in which the relaxation and creep moduli are obtained from the following expressions:

$$E(t) \approx [E'(\omega) - 0.4E''(0.4\omega) + 0.014E''(10\omega)]_{\omega=1/t} \tag{23}$$

$$D(t) \approx [D'(\omega) + 0.4D''(0.4\omega) - 0.014D''(10\omega)]_{\omega=1/t} \tag{24}$$

3 Experimental programme

3.1 Experimental equipment

In this work, the experimental part was conducted in a DMA-RSA3 Dynamo-Mechanical Analyzer by TA Instruments. The device is equipped with a temperature-controlled chamber to conduct experiments over a wide range of temperatures, from −60°C to 150°C, a load cell and an independent drive motor that can apply static and oscillating loads. A three-point bending tool and a three-point bending fixed tool were used for static and dynamic tests, respectively.

3.2 Study material

Interconversions were tested using a 2 mm thick polymethyl methacrylate (PMMA) as study material. The rectangular specimens were cut from the same material sheet with dimensions selected to suit each test, i.e., 40 × 10 mm for static tests and 40 × 5 mm for dynamic tests.

After experimentally demonstrating the influence of moisture content on the viscoelastic properties of the PMMA, see Fig. 1, the material was kept in an oven at 40°C for one week before starting testing.

3.3 Obtaining the PMMA moduli

The master curves for the relaxation modulus, creep modulus and complex modulus of PMMA were obtained by the principle of Time-Temperature Superposition Principle (TTS) (Lakes 1998; Williams et al. 1955) for a reference temperature of 40°C. For application of the TTS, the horizontal adjustment factors are obtained by the Williams-Landel-Ferry (WLF) equation (Ferry 1980) using the TA Orchestrator software (TA Orchestrator Help 2003). This procedure consists in overlapping the curves at each different temperature by a residual minimization algorithm using cubic spline interpolation to obtain the master curve after the corresponding WLF fit. The values of C1 and C2 for the WLF fit model are presented in Table 2 for each modulus. Figure 2 shows the relaxation modulus curves obtained for different temperatures. The parameters used in the different experiments are shown in Table 3.

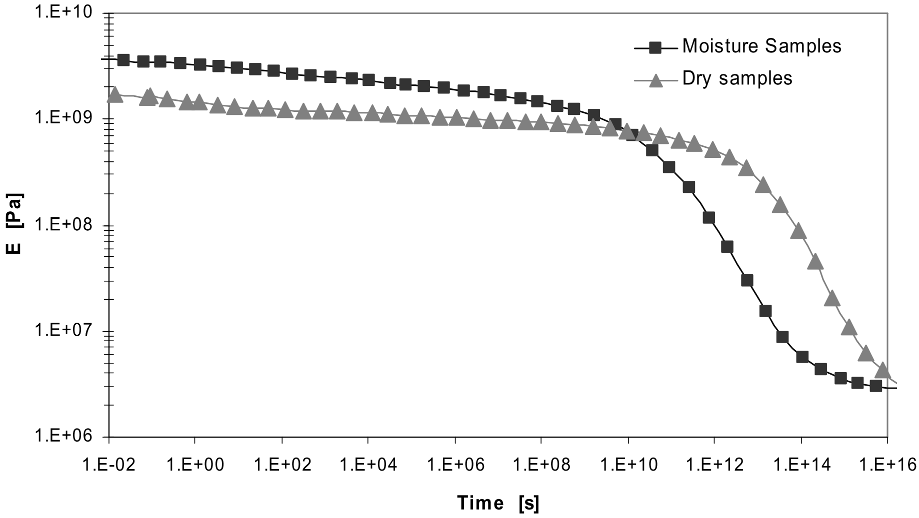

Fig. 1 Influence of moisture on the PMMA relaxation modulus

Table 2 WLF values fitted for the different moduli

	Relaxation	Creep	Complex
Reference Temperature	40	40	40
C1	−12.283	−8.15	−10.321
C2	−110.19	−115.39	−98.234

In order to apply the Prony-based conversions, the relaxation and creep compliance modulus were fitted with the generalized Maxwell and Kelvin models, (10) and (11), respectively. The values of the Prony series coefficients and the goodness of the fit for each modulus are presented in Table 4.

4 Analysis of results

After obtaining experimentally the different moduli of study material (PMMA), interconversions between them were carried out and compared, giving the following results.

4.1 Relaxation modulus

Figure 3 shows the relaxation curve obtained experimentally and that obtained from the creep modulus by the Park-Schapery conversion method. With this method, the relaxation modulus obtained from the conversion is lower than that obtained experimentally, so it gives less rigidity to the material. For a time of 10 s, therefore, the relative error when compared to the experimental curve is 8.5%.

As shown in Fig. 4, the relaxation modulus can also be obtained from the components of the complex modulus, by the Ninomiya and Ferry algorithm. In this case, the relative error between both curves for a time of 10 seconds is around 14.7%.

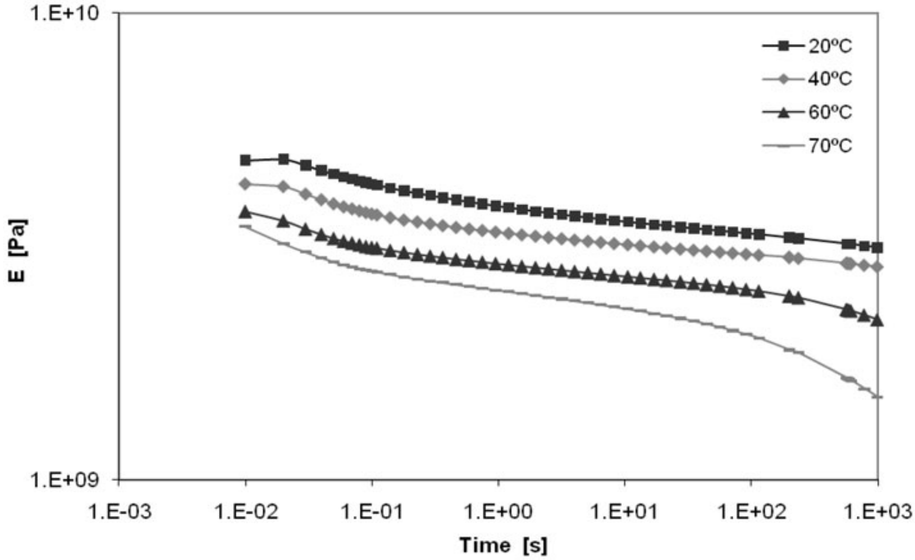

Fig. 2 Curves of the relaxation modulus at different temperatures

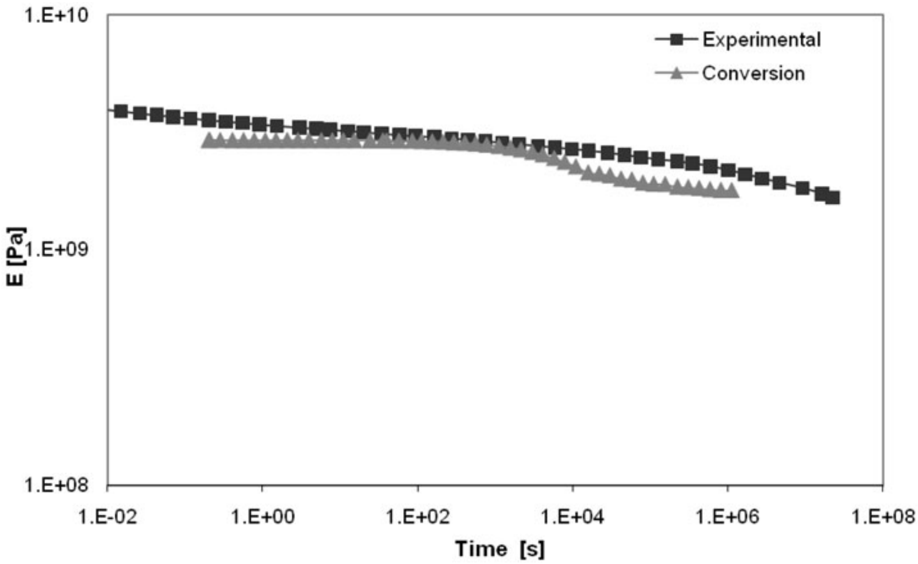

Fig. 3 Result of the conversion from creep to relaxation moduli

4.2 Creep modulus

In this case, the creep modulus obtained by the conversion is lower than the experimental one obtained in the entire domain studied. For a time of 10 s the relative error between both curves is around 21%.

Table 3 Experimental programme data

	Relaxation	Creep	Complex
N^{o} of tests	4	5	7
Temperature range	20–70°C	20–70°C	40–75°C
Duration/ω range	1000 s	1000 s	0.01–80 Hz

Table 4 Prony series coefficients for relaxation and creep moduli

	Relaxation		Creep	
Prony term	ρ_i	e_i	τ_j	d_j
1	7.58E−03	7.50E+08	9.42E−01	3.22E−10
2	8.54E−02	1.58E+08	4.46E+00	1.53E−09
3	9.62E−01	2.81E+08	2.11E+01	7.23E−09
4	1.08E+01	1.71E+08	1.00E+02	3.42E−08
5	1.22E+02	1.80E+08	4.74E+02	1.62E−07
6	1.38E+03	1.81E+08	2.25E+03	7.68E−07
7	1.55E+04	2.25E+08	1.06E+04	3.64E−06
8	1.75E+05	2.21E+08	5.04E+04	1.72E−05
9	1.97E+06	3.74E+08	2.39E+05	8.16E−05
10	2.22E+07	4.80E+08	1.13E+06	3.86E−04
$r2$ (goodness)	0.998		0.892	

Figure 5 shows the creep curve obtained experimentally and that obtained from the relaxation modulus by the Park-Schapery method.

4.3 Components of the complex modulus

The real component (storage) and imaginary component (loss) of the complex modulus are obtained by the Prony coefficients method, from the relaxation modulus obtained experimentally.

Figure 6 shows the results obtained for the storage component, E', giving rise to higher conversions than those obtained experimentally. At a frequency of 1 Hz the error between both curves is 8.5%.

Figure 7 shows the experimental and the conversion results for the loss component, E''. Here, higher discrepancies than in previous cases are observed, reaching 33% for a frequency of 1 Hz. This may be due to the fact that the experimental master curve was obtained as the envelope of the overlaying data from the different temperatures considered in the TTS process.

5 Conclusions

From the results obtained, the following conclusions can be given:

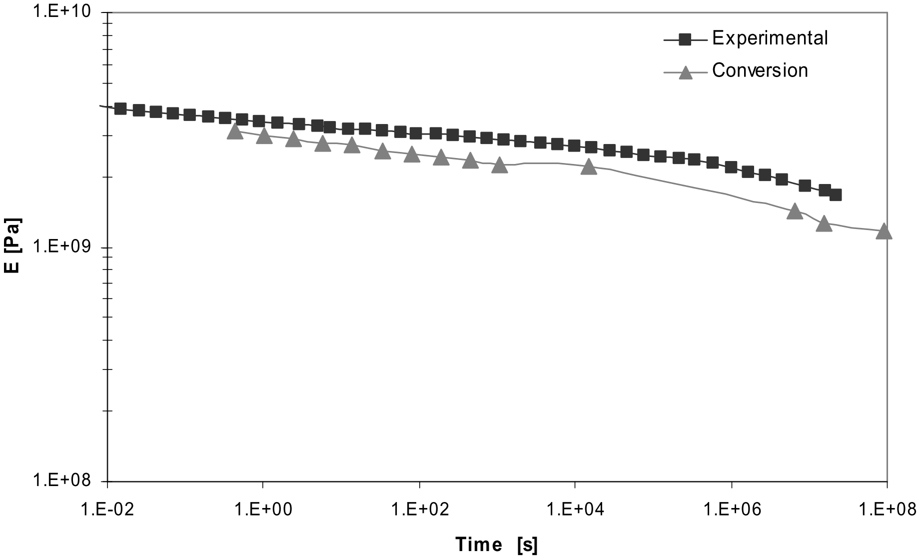

Fig. 4 Result of conversion from complex to relaxation moduli

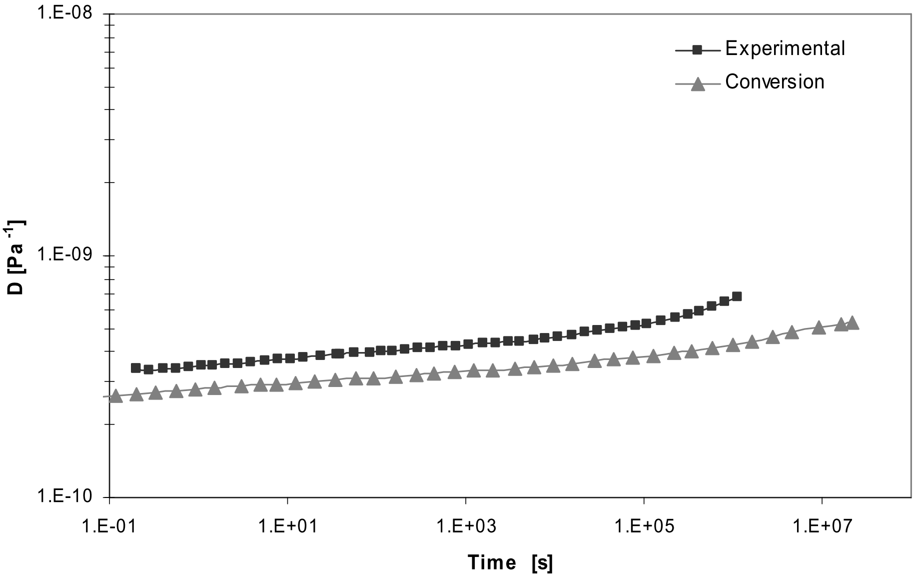

Fig. 5 Result of conversion from relaxation to creep moduli

1) Interconversion methods between the viscoelastic functions studied provide acceptable results, when compared to the scatter observed in the experimental results by testing PMMA.

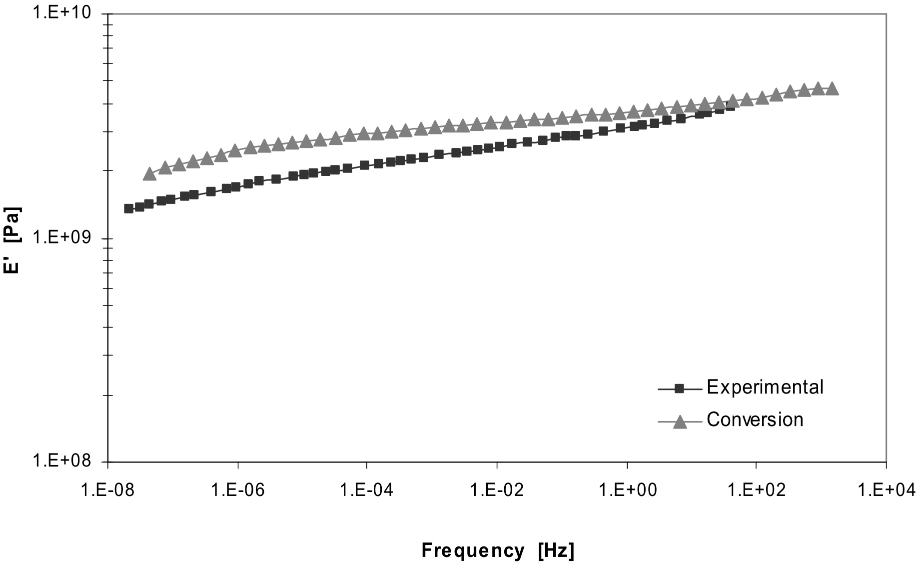

Fig. 6 Result of conversion from relaxation to storage moduli

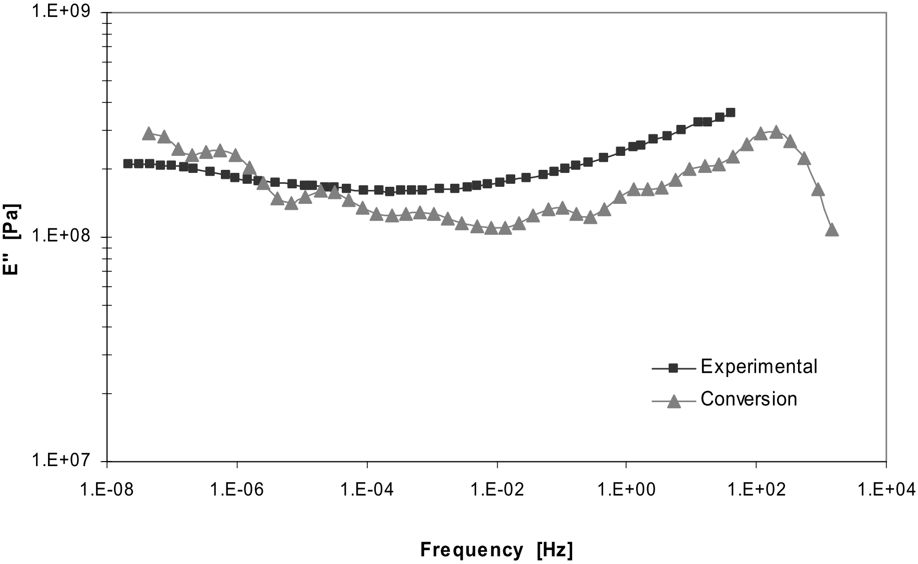

Fig. 7 Result of the conversion from relaxation to loss moduli

2) Since the relaxation tests are simpler to carry out, interconversion methods could provide a suitable way to obtain creep and dynamic moduli, for which testing is generally more complex.
3) The effect of moisture on viscoelastic characterization of polymers is an important factor that must be taken into account.

4) Application of interconversions is a simple methodology to obtain the different moduli. It would, therefore, be recommendable to increase experimental studies to other linear viscoelastic materials to establish its limitations.

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